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Publication Title:

DOUBLE ENCAPSULATION PROCESS AND FLAVORANT COMPOSITIONS  
PREPARED THEREBY

Abstract:

A flavorant composition which exhibit controlled release properties may be conveniently and economically prepared by a process involving (i) microencapsulating a flavoring agent in a microcapsule by coacervation, to obtain a first suspension in which coacervated microcapsules are suspended in a liquid; (ii) adding an edible solute to the first suspension, to obtain a second suspension, in an amount such that the content of the edible solute in the second suspension is 5 to 55 wt.% based on the total weight of the second suspension; and (iii) subjecting the second suspension to spray drying to obtain the flavorant.

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## INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

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<b>(21) International Application Number:</b> PCT/US96/16124 <b>(22) International Filing Date:</b> 11 October 1996 (11.10.96)  <b>(30) Priority Data:</b> 60/005,441 12 October 1995 (12.10.95) US 08/695,344 9 August 1996 (09.08.96) US  <b>(71)(72) Applicants and Inventors:</b> PORZIO, Michael, A. [US/US]; 9 Chesterfield Court, Monkton, MD 21111 (US). MADSEN, Michael, G. [US/US]; 4130 Glen Park Road, Baltimore, MD 21236 (US).  <b>(74) Agents:</b> KELLY, Richard, D. et al.; Oblon, Spivak, McClelland, Maier & Neustadt, P.C., 4th floor, 1755 Jefferson Davis Highway, Crystal Square Five, Arlington, VA 22202 (US).		<b>(81) Designated States:</b> AL, AM, AT, AU, AZ, BB, BG, BR, BY, CA, CH, CN, CU, CZ, DE, DK, EE, ES, FI, GB, GE, HU, IL, IS, JP, KE, KG, KP, KR, KZ, LK, LR, LS, LT, LU, LV, MD, MG, MK, MN, MW, MX, NO, NZ, PL, PT, RO, RU, SD, SE, SG, SI, SK, TJ, TM, TR, TT, UA, UG, UZ, VN, ARIPO patent (KE, LS, MW, SD, SZ, UG), Eurasian patent (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European patent (AT, BE, CH, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE), OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN, ML, MR, NE, SN, TD, TG).  <b>Published</b> <i>With international search report.</i>
<b>(54) Title:</b> DOUBLE ENCAPSULATION PROCESS AND FLAVORANT COMPOSITIONS PREPARED THEREBY  <b>(57) Abstract</b>  A flavorant composition which exhibit controlled release properties may be conveniently and economically prepared by a process involving (i) microencapsulating a flavoring agent in a microcapsule by coacervation, to obtain a first suspension in which coacervated microcapsules are suspended in a liquid; (ii) adding an edible solute to the first suspension, to obtain a second suspension, in an amount such that the content of the edible solute in the second suspension is 5 to 55 wt.% based on the total weight of the second suspension; and (iii) subjecting the second suspension to spray drying to obtain the flavorant.		

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TITLE OF THE INVENTION

DOUBLE ENCAPSULATION PROCESS AND FLAVORANT  
COMPOSITIONS PREPARED THEREBY

BACKGROUND OF THE INVENTIONField of the Invention:

The present invention relates to a process for producing encapsulated flavor systems which exist in the form of a coacervated flavor core microencapsulated in a spray-dried particle matrix. The present invention also relates to flavorant compositions produced by such a process. The present invention further relates to a new method of coacervation and the products produced by such a method.

Discussion of the Background:

Commercial encapsulation of flavoring materials is generally limited to spray drying and melt extrusion. Flavor encapsulation employing the spray drying process requires that the flavor, in the form of an aqueous emulsion with solubilized carrier solids, be fed into the spray dryer, atomized and dispersed into a heated air chamber plenum, dried, and collected. The resulting product is obtained as a fine particulate with lipid flavor droplets dispersed within the porous particle matrix. The carrier solutes used in the emulsion preparation are required not only to have emulsifying properties but also be bland, exhibit a high degree

of solubility with low intrinsic viscosity, be non-reactive with the flavor load while retaining volatile components, and exhibit stable powder properties once dried. In almost all commercial production formulas the carrier solutes of choice are usually selected for their emulsifying functionality and high degree of solubility.

It is well known by those skilled in spray drying processes that retention of volatiles is improved with increased dissolved solids levels in the aqueous phase of the emulsion. This requirement generally restricts spray drying encapsulation formulations to the use of highly water-soluble, modified starches, such as the octylsuccinate-derivativized modified starches, or gum arabic as the emulsifying, film-forming carrier polymer component. Soluble, inert carrier components such as sugars, corn syrup solids and maltodextrins are added to the aqueous flavor emulsion in order to increase solids levels, lower ingredient costs, increase yield, and improve product stability.

The spray drying encapsulation process is relatively simple, economical, and easily scaled to large production volumes. A major benefit of spray drying encapsulation relates to the broad range of flavors and flavoring systems which can be prepared. These flavorings include oil-soluble flavors, water-soluble compounds, natural extracts, single component flavor compounds, as well as complex compounded flavors having both water- and oil-soluble components.

The spray drying of flavors is well described in the art. G. Reneccius describes the control of a number of the process and carrier composition variables which lead to improved yields for the spray drying of orange oils, while also improving the stability of citrus terpenes to oxidation in the resulting product (see: Flavor Encapsulation, American Chemical Society Symposium Series #370, S. Risch and G. Reneccius, Eds. 1988, Chapter 7, which is incorporated herein by reference.). Among the key parameters identified are choice of emulsifying carrier, dissolved carrier solids levels, and control of inlet and outlet air temperatures within the drying chamber.

U.S. Patent No. 3,971,852 discloses the encapsulation of very high levels of an oil flavor in selected matrix compositions by spray drying. This patent discloses specific binary carrier compositions consisting of a polymer and polyol or sugar which allow the droplet matrix to retain its continuous, plastic film character during the initial drying stage, ultimately yielding particles characterized as having a glassy character and reduced porosity. Claims for high oil loads of up to 80% by volume as well as low levels of surface oil are made.

U.S. Patent No. 4,532,145 describes use of a binary spray drying carrier composition consisting of a low molecular weight component 90-500 Daltons (10-30%), and a higher molecular weight component 1000-6000 Daltons (70-90%) which are combined in

solution and employed as the carrier encapsulating media for spray drying and stabilization of volatile flavorings.

U.S. Patent No. 5,124,162 teaches the fixation of flavors by spray drying with a carrier composed of mono- or disaccharides (22-45% ), maltodextrin (25-50%), and a film-forming polymer (10-35%). A densified particle is obtained having a free flow bulk density of at least 0.50 g/cc with less than 20% voids in the particle.

U.S. Patent No. 5,087,461 teaches an encapsulation process consisting of an initial spray drying of a volatile flavor followed by melt extrusion of the spray-dried flavor in a carbohydrate matrix. The matrix composition consists of a chemically modified starch (40-80%), a maltodextrin (10-40%), corn syrup solids or polydextrose (5-20%), and mono- or disaccharide (5-20%) and flavor to obtain a solid, glassy encapsulation matrix.

While commercial spray drying encapsulation accounts for the vast majority of manufactured encapsulated flavors, one key limitation of these products is the lack of any controlled release functionality.

Coacervation encapsulation, a technology commercialized in the 1950s, yields true controlled release functionality and has found wide usage in the pharmaceutical, fragrance and specialty products industries. However the relatively high process costs, sensitive multi-step batch process, regulations limiting the



number of polymeric agents which can be used in food preparations, and the difficulty in dealing with encapsulates having both aqueous and lipid solubility properties has drastically limited the application of coacervation for flavor encapsulation in the food industry. A general discussion of these issues is provided by R. Versic in Flavor Encapsulation, American Chemical Society Symposium Series #370, S. Risch and G. Reneccius, Eds., 1988, Chapter 14, "Coacervation for Flavor Encapsulation," which is incorporated herein by reference.

Coacervation microcapsule systems can be generated in the form of simple coacervates, which are derived from a single polymer species in solution. Complex coacervates, which require the interaction of two distinct and oppositely charged polymer species, are also well characterized.

The coacervation process for flavor encapsulation consists of the following general steps: (1) dissolution of the polymer(s) at predetermined concentration(s) in aqueous solution(s); (2) emulsification of the flavor oil in the aqueous solution (and addition of the second polymer in the case of complex coacervation); (3) coacervation or phase separation of the polymer(s) by means of a change in temperature, pH, or dilution, or by addition of a water-miscible co-solvent or salt to generate a controlled phase separation with the concomitant association of the enriched polymer phase around the flavor oil droplet; (4) optionally chemically cross-linking the hydrated coacervated



polymer phase ; (5) decanting the liquid media and washing the retained microencapsulated product free of undesirable solutes; and (6) optionally drying the recovered capsules.

The coacervation microencapsulation process has not been significantly applied in the flavor encapsulation field for a number of practical reasons. First, only water-insoluble flavorings can be easily encapsulated when utilizing an aqueous medium for polymer solubilization and flavor emulsification. This limitation results from the fact that the water-soluble flavor components will partition into the aqueous phase, not only changing the flavor profile of the retained encapsulated flavor oil but also interfering with interfacial surface tension dynamics involved in formation of the coacervating polymer layer around the flavor droplet. Secondly, the requirement of generating dilute polymer solutions with complex coacervation leads to handling large volumes of liquid media in a batch operation. Thirdly, the sensitive nature of the complex coacervation process can lead to scaling problems when attempting to go from laboratory to production volumes. While these limitations are well known in the coacervation encapsulation field, the ability of coacervation encapsulation to exhibit true controlled release properties in response to moisture, heat, and mechanical stress makes it a desirable encapsulation technology.

Issues relating to the commercial scale-up of microencapsulation processes have been reviewed in some detail by

V.A. Crainich, Jr. in "Microencapsulation: Scale-up Considerations and Production Technology", Drugs and Pharmaceutical Science, Volume 41, pp. 221-255 (1990), which is incorporated herein by reference. The drying of microcapsules is discussed. It is stated that a combination of drying systems is usually necessary to obtain dry, free-flowing microcapsules. Commercial drying systems that have been employed for this purpose include spray dryers, tower dryers, fluid-bed dryers, flash dryers, tray dryers, and rotary dryers in both batch and continuous configurations. Chemical agents utilized in the treatment of wet microcapsules before drying include the addition of surfactants, or drying aids such as silicates, talc, and starches which are employed as part of a combined system. The disclosed preferred system for drying microcapsules is the batch, fluidized bed dryer employing drying aids (pages 249-51 of the above reference.)

U.S. Patent No. 3,647,481 mentions coacervation encapsulation in relation to a series of aliphatic di- and tri-sulfides as flavoring compositions. In one Example, a flavor composition is encapsulated by complex coacervation and capsules obtained by spray drying. No disclosure of the spray drying process conditions or the use of carriers is given.

Preparation and compositions of coacervated encapsulated flavor oil capsules are disclosed in International Patent Application WO 93/19621. Flavor oils are microencapsulated by

coacervation, cross-linked, and partially dewatered.

International Patent Application WO 93/19622 discloses the preparation of heat-stable, fracturable, spray-dried oil microcapsules. The wet coacervate capsules are washed and dispersed in water to form a slurry, silicon dioxide is added as an anticaking agent, and the dispersed system is spray dried.

A coacervate consisting of a non-polar wall forming polymer and a polyelectrolyte polymer for encapsulation of a core material is disclosed in U.K. 1,071,169. Solutions of the non-polar polymer, such as methylcellulose, and the polyelectrolyte, such as sodium carboxymethylcellulose or gum arabic, are treated with ammonium or sodium sulfate, coacervation is initiated, and capsules are collected and dried in a hot air stream. No spray drying or addition of drying carriers is taught.

H. Takenaka, Y. Kawashima, and S.Y. Lin, in J. Pharmaceutical Sciences, Volume 69, No. 5, pp. 513-516 (1980), describe a study in which gelatin-gum acacia coacervate microcapsules containing sulfamethoxazole were prepared. Experimental drying procedures describe both solvent dehydration and spray drying of the coacervate. Spray drying was performed by suspending the coacervate microcapsules in distilled water and pumping the water-coacervate slurry into the spray drier.

U.S. Patent No. 3,872,024 discloses the use of inorganic polymeric solutes to induce liquid-liquid phase separation of water-soluble polymers. A sodium polyphosphate solution is mixed

with a gelatin solution at elevated temperatures, the pH is adjusted to 6.8, and the polymer-inorganic polymer interactions are initiated. An encapsulant liquid is added, and the solution is allowed to slowly cool to develop the coacervate at room temperature. The system can then be cooled to 5°C to harden the gelatin microcapsule wall which is crosslinked with glutaraldehyde. Capsules are collected by filtration, washed, and dried by conventional means. There is a brief reference to hot air drying of the recovered capsules but no details are provided.

U.S. Patent No. 3,567,650 discloses the use of aqueous solutions of methylcellulose as the wall forming polymer in a coacervation process. The methylcellulose, in the presence of a complimentary hydrophilic polymer such as dextran, polyvinylpyrrolidone, polyvinylalcohol or gum arabic, forms the coacervate encapsulate with a variety of materials including lemon oil, aspirin, menthol and various drugs. In the disclosed preferred embodiment, the polydispersed aqueous coacervate system is brought to 50-60°C inducing wall formation by the methylcellulose to assist in recovery of the microcapsule. After removing excess water at the noted elevated temperatures, the microcapsules were dried using conventional techniques.

Thus, it is clear that flavorant compositions obtained by both spray drying and coacervation, although each offering advantages to the food industry suffer from notable drawbacks.

Accordingly, there is a need for flavorant compositions which are free from such drawbacks. Additionally there is a need for a process to generate such encapsulated flavors. There also remains a need for new methods to effect coacervation.

#### SUMMARY OF THE INVENTION

Accordingly, it is one object of the present invention to provide novel flavorant compositions.

It is another object of the present invention to provide novel flavorant compositions which are economical to prepare.

It is another object of the present invention to provide novel flavorant compositions which exhibit controlled release properties.

It is another object of the present invention to provide novel flavor compositions which are in the glassy state.

It is another object of the present invention to provide a process for preparing such flavorant compositions.

It is another object of the present invention to provide a process for preparing such flavorant compositions which is economical carry out.

It is another object of the present invention to provide a new method of encapsulating a flavor by coacervation.

These and other objects which will become apparent during the following detailed description have been achieved by the

inventor's discovery that such flavorant compositions may be prepared by a process comprising:

(i) microencapsulating a flavoring agent in a microcapsule by coacervation, to obtain a first suspension in which coacervated microcapsules are suspended in a liquid;

(ii) adding an edible solute to the first suspension, to obtain a second suspension, in an amount such that the content of said total edible solute in said second suspension is 5 to 55 wt.%, based on the total weight of said second suspension; and

(iii) subjecting said second suspension to spray drying.

#### BRIEF DESCRIPTION OF THE DRAWINGS

A more complete appreciation of the invention and many of the attendant advantages thereof will be readily obtained as the same becomes better understood by reference to the following detailed description when considered in connection with the accompanying drawings, wherein:

Figure 1 is a photomicrograph of a coacervate of orange oil prepared by utilizing a hydroxypropylmethylcellulose maltodextrin system. The coacervate was diluted in additional 35% maltodextrin solution to show the botryoid form as prepared in Example 1 (at 400x magnification); and

Figure 2 is a photomicrograph of the double encapsulation product of Example 1 (xylene mount at 200x magnification).



DETAILED DESCRIPTION OF THE PREFERRED EMBODIMENTS

The present process involves first preparing a coacervated flavor microcapsule in a liquid medium. The flavor can be a compounded oil flavor, an essential oil, an oleoresin, an amphiphatic flavor dissolved in or diluted in a lipophilic flavor solvent such as triacetin, medium chain triglycerides or vegetable oil, or a natural flavor extract which contains water-soluble components. Specific examples of preferred flavoring agents include essential oils such as the citrus oils (lemon, lime, orange, tangerine), anise oil, caraway oil, cinnamon oil, pepper oil, clove oil, fennel oil, ginger oil, peppermint oil, rosemary oil, spearmint oil; spice oleoresins derived from allspice, basil, capsicum, cinnamon, cloves, cumin, dill, marjoram, nutmeg, paprika, black pepper, rosemary and tumeric; allium oils (onion, garlic, chive), butter oils, cheese flavors, compounded natural and artificial lipid-soluble flavors, botanical extracts, natural and synthetic flavor constituents such as alcohols, ketones, esters, aldehydes and fatty acids, as well as oil extracts of reaction flavors, fruits and vegetables.

The flavor is emulsified in an aqueous polymer solution to obtain dispersed flavor droplets. The coacervating water-soluble polymer can be chosen from the group of food grade materials including gelatin, gum arabic (acacia), methylcellulose, hydroxypropylcellulose, propylene glycol alginate, hydroxypropylmethylcellulose, sodium carboxymethylcellulose,



sodium alginate, xanthan gum, gum tragacanth, locust bean gum, carageenan(s), modified food starch(s), sodium polyphosphates, low methoxy pectin, pectin, and other water soluble food polymers as noted by R. Versic in Flavor Encapsulation, S. Risch and G. Reneccius, Eds. ACS Symposium Series #370, (1988) Washington, D.C., pg. 130, which is incorporated herein by reference.

The coacervation process may be carried as described in C. Thies in Encyclopedia of Polymer Science and Engineering, 2nd Ed., John Wiley and Sons, Inc., New York, vol. 9, pp. 724-731 (1987) and in C. Thies, "Physiochemical Aspects of Microencapsulation," in Polymer-Plastic Technology and Engineering, vol. 5(1), pp. 1-22 (1975), and in U.S. Patent Nos. 2,800,457, 2,969,331, 3,043,782, and 3,567,650, all of which are incorporated herein by reference.

Typically, the flavoring agent in a simple coacervate system is dispersed in the warm aqueous polymer solution in an amount of 1 to 20 wt.%, preferably 5 to 15 wt.%, based on the total weight of the original initial aqueous solution.

A simple coacervate may utilize a hydrophilic polymer such as gelatin. For this coacervate system, a 5 to 15 wt.% gelatin solution is prepared and held at a temperature above 40°C. Following the emulsification of the flavoring in the heated gelatin solution, a phase separation inducing agent is added, and the mixture is agitated at the desired temperature until the coacervation is complete. To those skilled in the art, it is

well known which specific coacervating or phase separation inducing agents may be employed for simple coacervates of water-soluble polymers. The use of water-miscible solvents such as ethanol, isopropanol, and acetone are well characterized. Salting out agents such as sodium sulfate and sodium polyphosphate are also routinely used. (see Theory and Practice of Industrial Pharmacy, L. Lachman, H. Lea and J. Kanig, Eds., pgs. 412-429, Lea and Feiberger, Philadelphia, 1988, which is incorporated herein by reference).

For preparation of complex coacervates, the preferred systems are gelatin-gum arabic, gelatin-sodium alginate, or gelatin-sodium polyphosphate. In the case of gelatin-gum arabic complex coacervate systems, the concentration of the initial gelatin polymer solution is generally 1.4 - 15 wt.%, and, similarly, the concentration of the initial gum arabic polymer solution is generally 1.4 to 15 wt.%. Following the emulsification and combination steps, the gelatin-gum arabic solution is diluted to a preferred final concentration of 1.2 to 2.5 wt.% for each polymer. The gum arabic solution is generally used to emulsify the flavor oil. The flavor oil is utilized in an amount such that the ratio of oil to polymer is from 1:1 to 100:1. Then the gelatin polymer solution is added to the emulsion while the temperature of the solution is initially maintained above the gelation temperature of the gelatin (40 to 50°C). The gelatin and gum arabic solutions are combined in an

amount such that the weight ratio of gum arabic to gelatin is 1.5:1 to 1:1.5, preferably about 1:1. The pH is then adjusted to 3.8-4.3 with dilute acid. The mixture is diluted with distilled water to yield a final solution concentration of 1.0 to 2.5 wt.% and cooled slowly to ambient temperature and maintained. Following formation of the complex coacervate shell around the flavor droplet, the solution can be brought to 5-10°C and a cross-linking agent such as glutaraldehyde added to insolubilize the core wall.

Although the coacervated microcapsules may be separated and washed prior to mixing with the edible solute, the spray drying of the coacervate can be made more efficient and result in increased recovery of the microcapsules if the edible solute is added to the original microcapsule suspension. The choice of edible solute material must meet the general criteria of exhibiting good water solubility, extremely bland taste, yield free-flowing and non-caking powder in the dried form, be non-crystallizing, and be non-reactive to the microcapsule shell and flavor components. The edible solutes which meet all the criteria include: maltodextrins 5-15 DE, corn syrup solids 20-42 DE, modified corn starches (n-octylsuccinate modified starch), sodium hexametaphosphates, sodium polyphosphates, citric acid-sodium citrate (binary mixtures), hydrolyzed gelatin, polydextrose and mono- and disaccharides. Other soluble, functional food polymers which may optionally be added as

minority components to the bulk carrier solutions as cosolutes, where compatible, include proteins such as gelatins(s), dairy proteins and isolates such as casein, whey proteins, and lactoalbumins; soy proteins, corn proteins; modified celluloses such as methylcellulose, hydroxypropylmethyl cellulose, carboxymethylcellulose, and hydroxypropylcellulose, gums and hydrocolloids such as xanthan, guar, locust bean, acacia carrageenan(s), alginate(s) and pectin(s) among others. In choosing the solute system, the primary criteria will be ease of solubility and stable powder properties. In many instances, compatible mixtures of soluble components may be utilized. Other applications will dictate the choice of edible solutes. When using sodium polyphosphates, it is preferred to use a maltodextrin in approximately equal levels to assist in retaining a free-flowing powder. When employing octylsuccinate modified starch, the use of the sodium citrate or citric acid-sodium citrate mixtures as the neutralizing agent to reduce the normally acidic character of the dissolved solids media is preferred.

In complex coacervation systems, the use of citric acid-sodium citrate buffer as a pH adjusting agent yields an additional advantage to the process. Additional edible solute materials can be then chosen from the materials cited above.

The use of hydrolyzed gelatin as an edible solute component may be employed where glutaraldehyde has been used for the crosslinking of the coacervate shell wall. Addition of 2-20 wt.%

of hydrolyzed gelatin to the dissolved solid will react with any unreacted glutaraldehyde remaining in the aqueous solution.

Typically the edible solute is added to the first suspension containing the coacervated microcapsules in an amount of 5.0 to 55 wt.%, preferably 20 to 45 wt.%, based upon the total weight of suspension including flavor oil and microcapsule wall.

When utilizing the double encapsulation process, citrus oils, spice oils and oleoresins are easily processed as the flavor encapsulate. Following coacervation and crosslinking, the microcapsules can be decanted, washed with distilled water, and resuspended in a pre-prepared solution of edible solute. Alternatively, when the core flavoring system contains limited quantities of water-soluble components, a partitioning response will occur during the emulsification step as the water-soluble components migrate into the aqueous phase from the dispersed lipid droplets. In these cases, the original aqueous medium used in the coacervation step can be retained with its soluble flavor components. Then the addition of solid edible solutes to the original encapsulation solution is preferred. An added benefit accrues to the spray drying step with the added low-molecular weight solids which increase retention of the water soluble volatiles. Proper selection of the added low-molecular weight solid can yield a matrix in the glassy state further enhancing long term retention of the volatile water-solubilized flavoring components.

In another embodiment, lipid-soluble flavor fixatives such as waxes and ethylcellulose can be combined with the lipid encapsulant before the emulsification step to retard flavor transport to the aqueous phase and improve flavor release in the final applications. The use of oil densifying agents such as brominated vegetable oils or ester gums, employed in the densification of the drink oil flavorants, can also be added to the flavor oil before coacervation step.

After the addition of the edible solute, the mixture is then spray dried. Any conventional spray drying apparatus may be used.

The addition of the edible solutes to the coacervated microcapsule aqueous suspension will increase the density of the aqueous phase. This can result in a "creaming" of the microcapsules prepared from lower density oils. While continuous agitation will redisperse the flocculated layer, low shear pumping of the aqueous suspension through extended lengths of the tubing leading to spray drier nozzle can lead to reflocculation, separation and disproportionation within the feed stream. To counter this effect, it is recommended that the coacervate fluid reservoir be placed in close proximity to the spray drier nozzle inlet. The use of in-line mixers and reduced tubing diameters to increase fluid shear will ameliorate separation of the microcapsules during pumping. Other atomizing nozzle and spray



drying systems such as used for the spray drying of cheese or hydrolyzed vegetable powders may also be employed.

The breadth of applications of this microencapsulation technology can be expanded into many other areas. For example, in the encapsulation of savory flavors, salt would normally be used as a flavor enhancer. In those cases, sodium and potassium chloride may be employed as one of the coacervation-inducing solutes and be retained in the second suspension, and ultimately, the spray dried product.

In the pharmaceutical industry, the need for additional controlled release microencapsulation systems could easily make use of this double encapsulation process with water-insoluble bioactive agents, or pharmaceutical materials which can be dissolved oil. Methylcellulose and hydroxypropylmethylcelluloses have been extensively employed as a hydration-retarding, control release agent in tablet formulations. With the double encapsulation product the methylcellulose and hydroxypropylmethylcellulose coacervate can be prepared, surrounding the discrete pharmaceutical agents and extending the control release functionality in standard tableting formulations. Other additional benefits of the double encapsulation process using the methylcellulose-maltodextrin simple coacervate system would include the increase in recovery of extremely expensive pharmacological materials, in addition to the ability to produce



homogeneous amorphous or glassy powders under sterile drying conditions.

In another embodiment, the present invention provides a simple coacervate system based upon a specific coacervation response of methylcellulose or hydroxypropylmethylcellulose polymer solutions. These polymer solutions have been found to form a coacervate upon addition of specific soluble, edible, carbohydrate oligomers. These carbohydrate oligomers are characterized as having Dextrose Equivalents of D.E. 2-42, which correspond to the maltodextrins (D.E. 1-15) and to corn syrup solids (D.E. 20 -42). The coacervation of the methylcellulose (and hydroxypropylmethylcellulose) is believed to result from interactions with the carbohydrate oligomers, i.e. the Dobry effect.

The flavor oil, in ratios of 0.5 to 80 parts flavor oil to one part polymer, is emulsified in the surface-active methylcellulose polymer solution made up as 0.5 to 6.0 wt.% polymer at ambient temperature. A carbohydrate co-solute, preferably maltodextrin or in a more limited instance corn syrup solids, is added slowly preferably in the solid form with continuous stirring until a phase separation is induced. In an alternative embodiment, a concentrated solution of maltodextrin (30-55 wt.%) can be slowly added with continuous stirring. Using a 10 D.E. maltodextrin, this phase separation is observed at approximately 18 wt.% added maltodextrin with methylcellulose (or

hydroxypropylmethylcellulose) present at a concentration of 2 wt.% in the original polymer solution.

The methylcellulose or hydroxypropylmethylcellulose can be of various substitution character and viscosity grades. These materials are commercially available from the Dow Chemical Company as the product Methocel®, in the form of methylcellulose (A series) or hydroxypropylmethylcellulose (E, F, J, K series) which are comprised of varying molecular weights and are referenced in terms of their solution viscosities. The upper practical concentration of the Methocel® material is determined by the limiting intrinsic viscosity of the polymer solution for practical emulsification of the flavor oil.

The response of methylcellulose solutions to the presence of other dissolved solutes is discussed briefly in the Dow Chemical Company Technical Handbook "METHOCEL Cellulose Ethers." In this technical brief, the tolerance of aqueous solutions of Methocel® to salts and sugar are noted at specific levels. With 100 ml of an aqueous 2% solution of the various Methocel® materials, 65 to 120 grams of sucrose will cause the polymers to phase separate. This response is explained in terms of the high concentration of the sugar solute competing for the water required to solvate and keep the polymer in a hydrated state. The concentrations of added electrolyte salts required to salt out the hydrated methylcellulose polymers under similar experimental conditions are also described. Maltodextrins with their larger average

molecular weights exhibit phase separation inducing responses at much lower concentration levels and are more likely to be polymer-polymer interactions.

The methylcellulose or hydroxypropylmethylcellulose flavor coacervate is characterized as a dispersion containing individual droplets of flavor surrounded by the enriched polymer phase as well as botryoid clumps of the encapsulated flavor oil droplets. The coacervated droplets prepared in Example 1 are shown as formed in the aqueous phase in Figure 1.

After the coacervation step is complete, addition of a water-soluble carrier solute will improve spray drying yield and drying efficiency in the production of the double encapsulation product. The dried particles are obtained in the form of a carrier matrix with interdispersed flavor droplets surrounded by a concentrated methylcellulose coacervate film. Figure 2 is a photomicrograph of the spray-dried double encapsulated coacervate as prepared in Example 1.

The polymer-polymer interactive response of other water-soluble, hydrophilic food polymers in solution with maltodextrin were evaluated. Solutions of modified cellulose such as carboxymethylcellulose of varying viscosities; gums and hydrocolloids such as guar, locust bean, xanthan, sodium alginate, algin, propyleneglycol alginate, pectin, low methoxy pectin, tragacanth, arabic; n-octylsuccinnalated starch, and gelatin were prepared at 1 wt.% or 2% levels. Then maltodextrin

was added reaching 20 wt.% and 30 wt.% levels in the presence of the prehydrated aqueous polymers. Only gelatin showed a limited phase change response. None of the other above-listed polymers interacted with the equivalent or higher concentrations of maltodextrin.

Other solutes that have been found to generate a coacervate with the methylcellulose polymers are the sodium (or potassium) polyphosphates. Suitable polyphosphates include sodium polyphosphate, glassy, sodium or potassium tripolyphosphate, and sodium hexametaphosphate (commercial source FMC). The mechanism involved is the classical salting out response as noted above which has been employed for coacervation with a number of water-soluble polymers as disclosed in U.S. Patent No. 3,872,024, or U.S. Patent No. 2,800,458 and in U.K. 1,071,169.

In the double encapsulation embodiment where the initial coacervation step utilizes a polyphosphate solute, maltodextrin is added to the microcapsule-phosphate dispersion to obtain a free-flowing, stable spray dried product. The use of polyphosphate alone followed by spray drying of dispersed capsules in the polyphosphate solution will result in the capsules sticking to the spray dryer chamber walls and severe losses of product.

In an alternative embodiment, a mixture of maltodextrin-sodium polyphosphate powder is preblended and added as the coacervation inducing solute. The preferred ratio of the mixture

being  $\geq 1:1$  maltodextrin:polyphosphate. The resulting spray dried coacervate powder product will be obtained as a stable free-flowing powder.

In most drying processes involving complex coacervation microcapsules, the microcapsules are separated from the original process solution, washed and suspended in water, silicon dioxide optionally added, and the capsules dried in a fluidized bed drier. The present double encapsulation process will work equally well with the complex coacervate systems. For those cases, the recovered capsules can be crosslinked, washed, suspended in 30-40 wt.%, dried solids basis (dsb) maltodextrin solution and spray dried. Alternatively the original reaction solution can be retained, carrier solids added, and the system spray dried.

For formation of the simple methylcellulose coacervate, the preferred carbohydrate co-solute, e.g. the maltodextrin, functions not only as the coacervate inducing oligomer but also as a spray drying process aid. This use results in increased recovery of the microcapsules, and a free flowing, non-caking powder product. The final total solid of the second suspension system for spray drying is typically in the range of 30-50 wt.%. Following addition of the maltodextrin and coacervation, other selected solids can be added to increase dissolved solids levels of the solution preceding the spray drying. These additional solute materials must meet the general criteria of exhibiting

high water solubility and low intrinsic viscosity, being extremely bland, being non-reactive to the microcapsule shell and flavor core, as well as yielding free-flowing, non-caking and non-crystallizing powders in the dried form. Edible solute materials and mixtures thereof which meet all these criteria include corn, potato and tapioca derived maltodextrins (5-15 D.E.), other dextrans, corn syrup solids (20-42 D.E.), modified corn starches (n-octylsuccinate modified starch), sodium hexametaphosphates, sodium polyphosphates, citric acid-sodium citrate (binary mixtures), polyols such as mannitol, lactitol and sorbitol, polydextrose, hydrolyzed gelatin, and mono- and disaccharides individually and as mixtures. In many instances, compatible mixtures of lower molecular weight carbohydrates such as corn syrup solids and maltose will be added to the maltodextrin solution when formation of a glassy state is desired with the spray dried product. Other soluble food polymers which may be added as minority components to the bulk carrier solutions as co-solutes, where compatible, include proteins such as gelatins, dairy proteins and isolates such as casein, whey proteins, and lactoalbumins; soy proteins, corn proteins; low viscosity gums and hydrocolloids. When employing the octylsuccinate modified starch, the use of sodium citrate or citric acid-sodium citrate mixtures as a neutralizing and buffering agent to reduce the acidic character of the dissolved solids media is preferred.



Other features of the invention will become apparent in the course of the following descriptions of exemplary embodiments which are given for illustration of the invention and are not intended to be limiting thereof.

#### EXAMPLES

##### Example 1.

A simple coacervate was prepared as follows: a 2.0 liter solution of 4.0 wt.% hydroxypropylmethylcellulose (Dow Chemical, Methocel E15) is prepared at ambient temperature and 100 grams of an orange oil (Citrus and Allied, single fold) is emulsified by slow addition to the polymer solution using an Arde-Barinco laboratory homogenizer at a low power setting. Following emulsification of the orange oil, 700 grams of 10 D.E. maltodextrin solids (American Maize, Lodex-10) are added slowly with continuous agitation over a 30 minute period. At approximately 20% added maltodextrin (total solids basis), a phase change is noted as the initial formation of a flocculated dispersion. The remaining maltodextrin is slowly added until the total final level of 35 wt.% (total solids basis) is reached. The orange oil suspension is stirred gently at ambient temperature to keep the coacervate from "creaming" for an additional hour. Then the orange oil coacervate dispersion in the maltodextrin solution is fed into a pilot plant Niro spray drier set with the inlet air temperature set at 390°F and outlet



temperature of 201°F at a rate of 2.5 lbs/hr and spray drying completed. Total solids recovered are 60% based upon components (oil-methylcellulose-maltodextrin) of the system. The product is obtained as a free-flowing amorphous powder with a particle density of 1.15 g/cc.

Example 2.

A coacervate was prepared as follows: A 1.0 liter solution of 6.0 wt.% methylcellulose (Dow Chemical, Methocel A15LV) was prepared and held at ambient temperatures. Then 73 grams of a compounded garlic flavor oil was slowly added and an emulsion formed using an Arde-Barinco laboratory homogenizer set at low power. Following the emulsification, 600 grams of a 1:1 dry blend mixture maltodextrin:sodium hexametaphosphate was slowly added with continuous stirring over a period of 30 minutes. During addition of the solids, a phase change is noted. The coacervated flavor is held with continuous stirring for an additional 2 hours. The suspension of the coacervated garlic oil is continually stirred and fed at 2.5 lbs/min into a pilot plant Niro spray drier set at inlet air temperature of 380°F and outlet temperature of 199°F. The double encapsulated product was obtained as a free-flowing powder. DSC analysis shows the powder to be in a glassy state with a Tg of 48°C.

Example 3.

A coacervate was prepared as follows: A 1.0 liter solution of 2.0 wt.% hydroxypropylmethylcellulose (Dow Chemical, Methocel F50) was prepared and held at 23°C. Then 72.6 grams of a compounded oil-soluble butter flavor containing approximately 20% of a water soluble flavoring component, diacetyl, is slowly added and an emulsion formed using an Arde-Barinco laboratory homogenizer. After the emulsion has been prepared, the pale yellow color of the diacetyl is observed in the aqueous phase. Then 422 grams of solid maltodextrin (Lodex-10, American Maize Co.) was added slowly with continuous stirring. With the addition of approximately 200 grams of the total 422 grams maltodextrin, a phase change is noted as a flocculated oil phase. Then additional solute consisting of 211 grams of a mixture of citric acid-sodium citrate (pH ~7) is added to the solution. The coacervated flavor is stirred for an additional 1.5 hours. The suspension of the coacervated butter flavor is stirred continually and fed at 2.5 lbs/min into a pilot plant Niro spray drier set at inlet air temperature of 386°F and outlet temperature of 194°F. The double encapsulated product was obtained as a free-flowing powder which has a yellow hue. DSC analysis shows the powder to be in a glassy state with a Tg of ~ 58°C.

Example 4.

A coacervate was prepared as follows: A 1.0 liter solution of 6.0 wt.% hydroxypropylmethylcellulose (Dow Chemical, Methocel F50) is prepared and held at 23°C. Then 72.6 grams of a lemon oil (Citrus and Allied, single fold) is slowly added and an emulsion formed using an Arde-Barinco laboratory homogenizer. After the emulsion has been prepared, 600 grams of solid maltodextrin (Lodex-10, American Maize Co.) is added slowly with continuous stirring. The coacervated flavor is held for an additional 1.5 hours. The lemon oil coacervate suspension is stirred and feed at 2.5 lbs/min into a pilot plant Niro spray drier set at inlet air temperature of 374°F and outlet temperature of 209°F. The double encapsulated product was obtained as a free-flowing amorphous powder.

Example 5.

A complex coacervate was prepared as follows: Gelatin (Type A, 275 Bloom) 45.0 grams was dissolved in 440 ml of distilled water held at 50°C. Sodium carboxymethylcellulose (4.5 grams) was dissolved in 220 grams of distilled water at 50°C. The two solutions were combined and the solution cooled to 35°C. Then 360 grams of liquid vegetable oil containing 0.1% D&C Violet #5 Dye was employed as the core material. The colored oil was emulsified employing an Arde Barinco homogenizer set at 40% of full power for approximately two minutes. After the oil was

completely dispersed, an additional 2 liters of distilled water at 35°C was added, and the solution was cooled to ambient temperature and held for 2 hours. The solution was cooled to 10°C, and 5.6 grams of a 50 wt.% glutaraldehyde solution was added to cross-link the capsule wall. The sample was split into to equal batches and allowed to stir overnight.

One sample (1600 ml) was retained as a control. The second sample was brought to 40% added solids content by the slow addition of 246 grams of a 1:1 (wt.:wt.) mixture of 15 DE maltodextrin-sodium hexametaphosphate. Both samples were then spray dried in a pilot plant spray drier under identical pumping feed rates, nozzle rpm, inlet and collection air temperatures. The control sample was obtained as very porous powder in approximately 21% yield based on the original solids content and had a solid density of 0.98 g/cc. The double encapsulation sample was obtained as a free flowing powder in 31% yield (based upon coacervate) and 83% yield based upon total system solids. This material had a solid density of 1.32 g/cc. Evaluation of the encapsulated material by microscopy shows uniform spherical particles with interior coacervate cores as both single and multiple droplets within the macroparticle.

A series of dissolved solids were tested by spray drying the coacervate system as reported in Example 5. The response of the materials to the process and the resultant character of the double encapsulated solid products are given in Table 1:

TABLE 1

## RESPONSE OF COACERVATE-ADDED SOLIDS SUSPENSION TO SPRAY DRYING

Carrier #	Solutes Solids Added (40%)	Particle Density* (g/cc)	Spray Dried Product Character
1	(0%) Control	0.98	porous powder, limited recovery from dryer
2	(1:1) 15 DE Maltodextrin sodium hexametaphosphate	1.32	free flowing powder, spherical particles with uniform walls around core
3	15 DE Maltodextrin	0.83	free flowing powder, spherical macroparticle with uniform wall around core
4	24 DE Corn Syrup Solids	1.14	free flowing powder, larger individual particles
5	Maltose	1.22	Amorphous solid, large agglomerated particles, poor recovery in dryer
6	Sucrose/Glucose/Maltose (1:1:1)	1.29	adhesive solid, large agglomerated clumps of multiple particles
7	Citric Acid-Sodium Citrate (4:1)	1.58	Glassy solid (T <sub>g</sub> =40°C) Significant coating on drier wall, agglomerated particles.

Particle Density measurement reported as average of 5 trials per sample using Micromeritics AccPyc 1330 pycnometer

Example 6.

A complex coacervate was prepared as follows: 26.4 gm of Gelatin (Type A, 275 Bloom) was dissolved in 213.6 ml of deionized water by heating and holding the solution at 50°C. Then 26.4 gm of gum arabic was dissolved in 213.6 gm of deionized water also heated to 50°C. A core material consisting of 160 grams of a vegetable oil containing 0.05 wt.% FD&C Violet 2

dye was added with stirring to the gum arabic solution at 48°C. The gelatin solution was then combined with the emulsified oil - gum arabic solution with the temperature maintained at 48°C. Following several minutes of stirring, 1500 ml of deionized water heated to 49°C was added over a period of 5 minutes to the gum arabic-gelatin emulsion system. The pH is adjusted to pH  $\approx$  4.20 with dilute acetic acid. The system is stirred continuously and allowed to quiescent cool to ambient temperature over a 2 hour period. The system is then cooled to 10°C by placing the batch container in a cooling bath. The pH is adjusted to 6.8 by addition of a dilute sodium citrate solution, and 5 ml of a 50 wt.% glutaraldehyde solution added, and the system held at 10-11°C for an additional hour and allowed to warm to ambient temperature overnight. A 1200 ml aliquot of the coacervation solution was taken, and 400 grams of a 60:40 mixture 10 DE maltodextrin- maltose monohydrate was slowly added with mixing. The coacervate-carbohydrate solution was dried in a pilot plant spray drier with inlet temperature set at 381°F and an outlet temperature of 232°F. A fine powder exhibiting a uniform violet color was obtained. Microscopic examination shows the color intensity concentrated in the coacervated oil droplet with no indications of free oil droplets.

Example 7.

A complex coacervate was prepared according to the following procedure: 440 ml of a 1.4 wt.% gum arabic solution was prepared and used to emulsify 300 grams of an orange oil (Citrus and Allied, single fold) by homogenization with an Arde Barinco laboratory homogenizer. Then 440 ml of a 1.4 wt.% gelatin (Type A, 200 Bloom) solution at 36°C was added to the emulsified orange oil-gum arabic system also held at 36°C.

The solution was adjusted to pH 4.0 by dropwise addition of a 30 wt.% acetic acid solution and the coacervate allowed to form by holding the system at ambient temperature for 1 hour. Then 6.0 grams of a 50 wt.% aqueous glutaraldehyde solution was added to crosslink the coacervated shell phase. After standing under gentle stirring for 15 hours, the sample was divided into two lots. To one lot of approximately 1600 ml was slowly added with stirring 1052 grams of a 1:1 mixture of sodium hexametaphosphate-15 DE maltodextrin solids over a period of one-half hour. The two lots, control and solids added dispersion were spray dried in a pilot plant unit under identical process parameters. The recovered dried products were obtained as fine powders. The yield of recovered control sample was 11% on a total solids basis, while the double encapsulated sample yield was 58% on a total solids basis.

Obviously, numerous modifications and variations of the present invention are possible in light of the above teachings.



It is therefore to be understood that, within the scope of the appended claims, the invention may be practiced otherwise as specifically described herein.

CLAIMS:

1. A process for preparing a flavorant composition, comprising:

(i) microencapsulating a flavoring agent in a microcapsule by coacervation, to obtain a first suspension in which coacervated microcapsules are suspended in liquid;

(ii) adding an edible solute to said first suspension, to obtain a second suspension, in an amount such that the content of said edible solute in said second suspension is 5 to 55 wt.% based on the total weight of said second suspension; and

(iii) subjecting said second suspension to spray drying to obtain said flavorant composition.

2. The process of Claim 1, wherein said flavoring agent is selected from the group consisting of the lemon oil, orange oil, tangerine oil, anise oil, caraway oil, cinnamon oil, pepper oil, clove oil, fennel oil, ginger oil, peppermint oil, rosemary oil, spearmint oil, spice oleoresins derived from allspice, basil, capsicum, cinnamon, cloves, cumin, dill, marjoram, nutmeg, paprika, black pepper, rosemary and tumeric; onion oil, leek oil, chive oil, garlic oil, butter oils, cheese flavors, compounded natural and artificial lipid-soluble flavors, botanical extracts, natural and synthetic flavor constituents such as alcohols,

ketones, esters, aldehydes and fatty acids, and extracts of reaction flavors, fruits and vegetables.

3. The process of Claim 1, wherein said microencapsulation is carried out by simple coacervation.

4. The process of Claim 1, wherein said microencapsulation is carried out by simple coacervation utilizing methylcellulose or hydroxypropylmethylcellulose as a water-soluble polymer and a carbohydrate oligomer having a D.E. in the range of 2 to 42 as a cosolute phase-separation inducing agent in an aqueous media.

5. The process of Claim 1, wherein said microencapsulation is carried out by complex coacervation.

6. The process of Claim 1, wherein said flavoring agent is a flavor oil.

7. The process of Claim 1, wherein said edible solute is added in an amount such that the content of said edible solute in said second suspension is 20 to 45 wt.% based on the total weight of said second suspension.

8. The process of Claim 1, wherein said coacervation is carried out with (i) methylcellulose or hydroxypropylmethyl cellulose; and (ii) a maltodextrin (5 to 15 D.E.), corn syrup solids (20 to 42 DE), sodium polyphosphate, or mixtures thereof.

9. The process of Claim 1, wherein said edible solute is selected from the group consisting of mono- and disaccharides, corn syrup solids, maltodextrins, modified starches, hydrolyzed gelatin, polydextrose, polyols, citric acid, sodium citrate,

sodium and potassium chloride, sodium polyphosphates, and mixtures thereof.

10. A flavorant composition prepared by a process, comprising:

(i) microencapsulating a flavoring agent in a microcapsule by coacervation, to obtain a first suspension in which coacervated microcapsules are suspended in a liquid;

(ii) adding an edible solute to said first suspension, to obtain a second suspension, in an amount such that the content of edible solute in said second suspension is 5 to 55 wt.% based on the total weight of said second suspension; and

(iii) subjecting said second suspension to spray drying to obtain said flavorant composition.

11. The composition of Claim 9, wherein said flavoring agent is selected from the group consisting of the lemon oil, orange oil, tangerine oil, anise oil, caraway oil, cinnamon oil, pepper oil, clove oil, fennel oil, ginger oil, peppermint oil, rosemary oil, spearmint oil, spice oleoresins derived from allspice, basil, capsicum, cinnamon, cloves, cumin, dill, marjoram, nutmeg, paprika, black pepper, rosemary and tumeric; onion oil, leek oil, chive oil, garlic oil, butter oils, cheese flavors, compounded natural and artificial lipid-soluble flavors, botanical extracts, natural and synthetic flavor constituents such as alcohols, ketones, esters, aldehydes and fatty acids, and extracts of reaction flavors, fruits and vegetables.

12. The composition of Claim 10, wherein said microencapsulation is carried out by simple coacervation.

13. The composition of Claim 10, wherein said microencapsulation is carried out by simple coacervation utilizing methylcellulose or hydroxypropylmethylcellulose as a water-soluble polymer and a carbohydrate oligomer having a D.E. in the range of 2 to 42 as a cosolute phase-change inducing agent in an aqueous media.

14. The composition of Claim 10, wherein said microencapsulation is carried out by complex coacervation.

15. The composition of Claim 10, wherein said flavoring agent is a flavor oil.

16. The composition of Claim 10, wherein said edible solute is added in an amount such that the content of said edible solute in said second suspension is 20 to 45 wt.% based on the total weight of said second suspension.

17. The composition of Claim 10, wherein said edible solute is selected from the group consisting of mono- and disaccharides, corn syrup solids, maltodextrins, modified starches, hydrolyzed gelatin, polydextrose, polyols, citric acid, sodium citrate, sodium and potassium chloride, sodium polyphosphates, and mixtures thereof.

18. The composition of Claim 10, wherein said composition is in the glassy state.

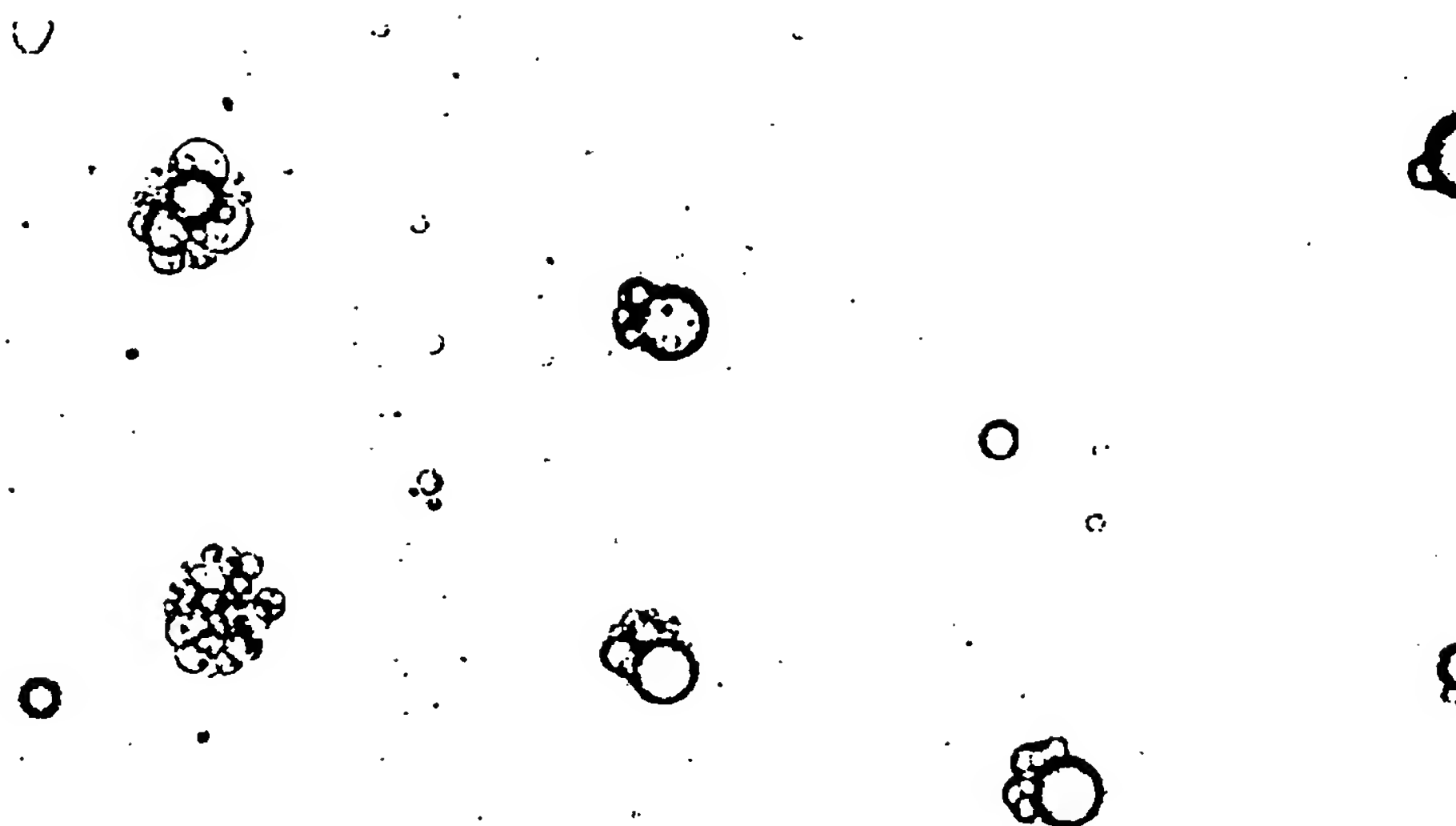
19. A method for encapsulating a flavorant, comprising:

(i) mixing said flavorant in an aqueous medium with a polymer selected from the group consisting of methylcellulose and hydroxypropylmethylcellulose to obtain a mixture; and

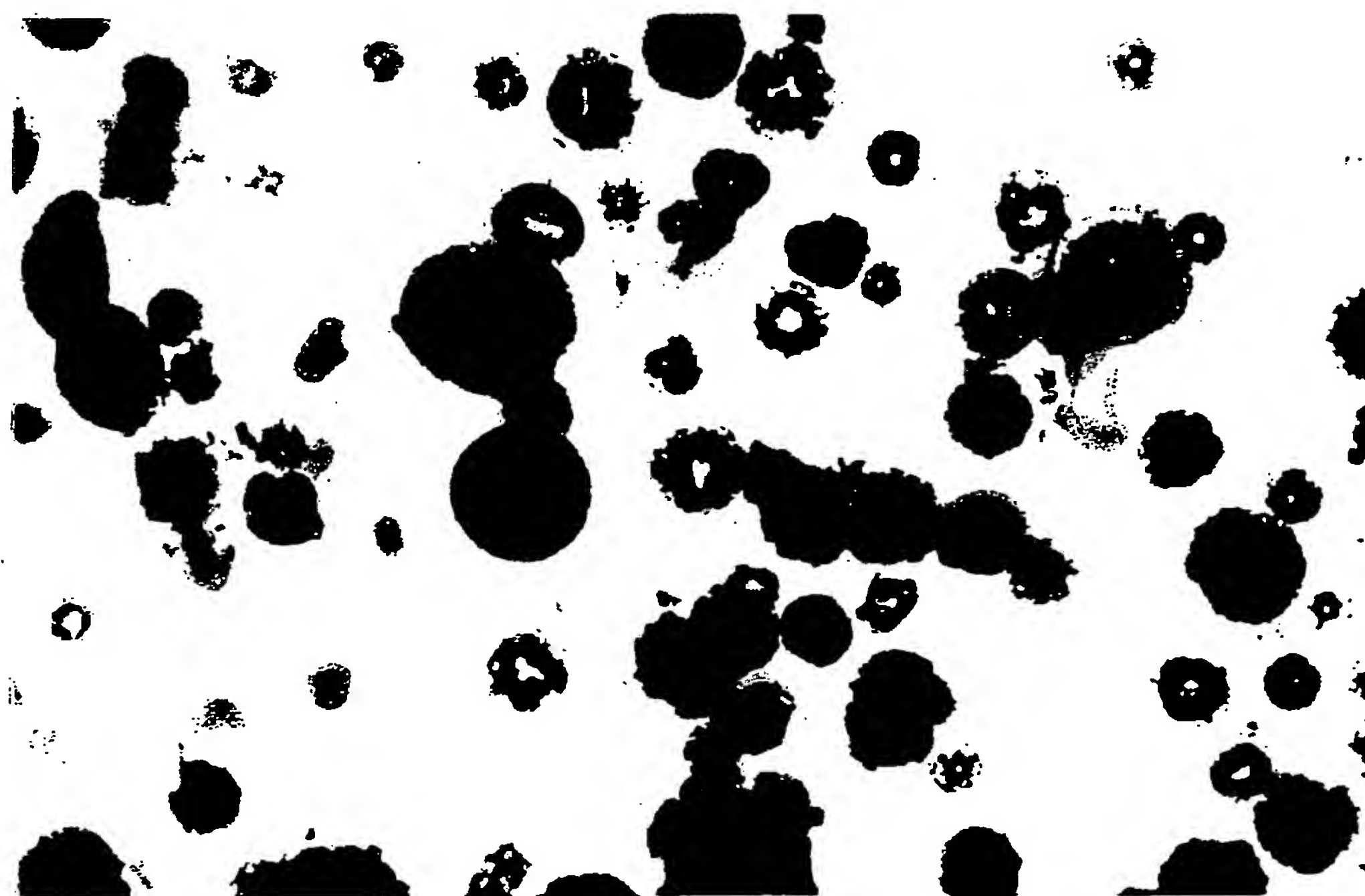
(ii) adding a phase-separation inducing agent selected from the group consisting of maltodextrins, corn syrup solids, and mixtures thereof to said mixture to effect coacervation.



**Figure 1**



**Figure 2**



## INTERNATIONAL SEARCH REPORT

International application No.  
PCT/US96/16124**A. CLASSIFICATION OF SUBJECT MATTER**

IPC(6) : A23L 1/221

US CL : 426/103

According to International Patent Classification (IPC) or to both national classification and IPC

**B. FIELDS SEARCHED**

Minimum documentation searched (classification system followed by classification symbols)

U.S. : 426/103, 89, 96, 98, 650, 651

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched  
NONEElectronic data base consulted during the international search (name of data base and, where practicable, search terms used)  
NONE**C. DOCUMENTS CONSIDERED TO BE RELEVANT**

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
Y	WO, 93/19622 ( PEARL ET AL. ) 14 October 1993 (14.10.93), page 5 lines 15-26, page 8 lines 1-20 and page 9 lines 3-5.	1-19
Y	US, A, 5,087,461 ( LEVINE ET AL ) 11 February 1992 (11.02.92), see col. 6 lines 1-68.	1-19

☐ Further documents are listed in the continuation of Box C.☐ See patent family annex.

* Special categories of cited documents:	*T	later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention
*A* document defining the general state of the art which is not considered to be of particular relevance	*X*	document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone
*E* earlier document published on or after the international filing date	*Y*	document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art
*L* document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)	*Z*	document member of the same patent family
*O* document referring to an oral disclosure, use, exhibition or other means		
*P* document published prior to the international filing date but later than the priority date claimed		

Date of the actual completion of the international search

09 DECEMBER 1996

Date of mailing of the international search report

15 JAN 1997

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